

# Adsorption, Interaction, and Manipulation of Dibutyl Sulfide on Cu{111}

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**ABSTRACT** This paper describes a low-temperature scanning tunneling microscopy (STM) study of a simple thioether, dibutyl sulfide, on a Cu{111} surface. The literature is full of data about thiol-based monolayers; however, relatively little is known about thioether self-assembly. Thioethers are more resilient to oxidation than thiols and offer the potential for control over nanoscale assembly in two dimensions parallel to the surface. Therefore, robust assembly schemes derived from thioethers may offer a new class of self-assembled systems with novel and useful properties. At a medium surface coverage and a temperature of 78 K, dibutyl sulfide grows in small, highly ordered islands in which the ordering is driven by both the molecule–surface dative bonds and intermolecular van der Waals bonding. Annealing to around 120 K allows diffusion and reordering of the molecules and the formation of large, very well ordered domains with little or no defects. We show high-resolution images of the molecular arrays and propose a model for their packing structure. These data suggest the potential use of thioethers for a variety of self-assembly applications that require control over molecular spacing parallel to the surface. We also show how the STM tip can be used to manipulate individual molecules within the ordered structures and that the arrays can act as a nanoscale abacus. The range of motion of the manipulated molecules inside a regular array reflects the potential imposed upon them by their neighbors.

**KEYWORDS:** thioether · dibutyl sulfide · Cu{111} · STM · self-assembly · molecular manipulation

Self-assembled monolayers (SAMs) have applications in many different fields, such as sensing, lubrication, corrosion inhibition, molecular electronics, patterning, and device self-assembly.<sup>1–13</sup> Thiol (RSH)-based SAMs account for roughly 50% of all SAM literature. Thiol SAM chemistry allows for excellent control over assembly in the one dimension perpendicular to the surface, but without top-down methods like micro-contact printing, thiol SAMs offer somewhat less control over lateral assembly.<sup>1,2,5,6</sup> They also display inhomogeneity in the form of etch pits and domain boundaries and are susceptible to oxidation.<sup>1,2</sup> The vast majority of thiol-based self-assembly has been performed on Au{111}, but for the purposes of this paper we will also discuss the self-assembly of thiols on Cu{111}.<sup>14–20</sup> Both theory and experiment have shown that these are com-

plex systems in which molecular adsorption reconstructs the top layer of the substrate and, depending on surface coverage, several ordered overlayer structures can be formed. Driver *et al.* used scanning tunneling microscopy (STM) to investigate the packing of both methanethiolate and octanethiolate on Cu{111} and found that both molecules formed small, ordered domains of either square or “honeycomb” structure.<sup>19,20</sup>

Thioethers (RSR) have a structure similar to that of alkanethiols but lie flat on the surface and offer the possibility for excellent control over assembly in the two dimensions parallel to the surface by varying the length of their tail groups. Thioethers also have a potential advantage over thiols in self-assembly, as they are less susceptible to oxidation.

The adsorption of ethers and thioethers has been studied on highly oriented pyrolytic graphite (HOPG). Padowitz *et al.* studied the assembly of both ethers and thioethers on HOPG.<sup>21,22</sup> These molecules were found to lie flat on the surface and assemble into regular domains in which the molecules aligned parallel to one another and were held together by van der Waals forces. The group also found that thioethers inserted into ether domains could be used as “chemical markers” and tracked in order to monitor diffusion in the monolayer. There are fewer than 10 papers in the literature in which the nanoscale assembly of thioethers on metals is discussed.<sup>23–31</sup> Previous STM studies are limited and have suggested that SAMs formed from thioethers are less ordered than thiol SAMs.<sup>25,26,30</sup> Hara and co-workers investigated the self-assembly of both dioctadecyl sulfide and tetrahydrothiophene on Au{111}.<sup>24,25</sup> They

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found that dioctadecyl sulfide physisorbed on Au{111} and did not lift the herringbone reconstruction.<sup>25</sup> Tetrahydrothiophenene, on the other hand, was found to chemisorb, lifting the herringbone reconstruction and forming regular domains with a few etch pits and some structural defects.<sup>24</sup>

In this study, we set out to investigate assembly of a simple thioether, dibutyl sulfide, on a Cu{111} metal surface. By performing this study in ultra-high vacuum (UHV) and at low temperatures (78 K), we aimed to discover how this molecule interacts with the bare surface at low coverage and how it self-assembles in the absence of impurities. We will demonstrate that it is possible to form very well ordered SAMs from dibutyl sulfide with none of the defects associated with thiol-based SAMs. We will discuss the structure and epitaxy of the molecular overlayer and demonstrate the effect of annealing on the packing structure. We also probe intermolecular interactions by performing molecular manipulation experiments with the STM tip. We recognize that assembly at 78 K is not necessarily practical; however, this study is aimed at elucidating the fundamental self-assembly characteristics of a simple thioether. These same rules should apply to longer-chain thioethers whose surface assemblies are stable at room temperature and in air.<sup>21,22,24,25,27</sup>

## RESULTS AND DISCUSSION

Figure 1 shows a typical STM image of the bare Cu{111} surface prior to deposition of molecules. Electron standing waves are seen emanating from a monoatomic step edge on the right side of the image. The depressions on the Cu terrace are point defects that also scatter the surface-state electrons and create standing waves of a circular pattern. The inset shows atomic resolution recorded on a flat part of the Cu surface. Typically the surface was cleaned and imaged, and once cleanliness was verified in a few different areas, dibutyl sulfide was dosed while the tip was scanning.

When a low coverage (0.03 monolayer (ML)) of dibutyl sulfide was deposited on the surface at 78 K, all molecules were found to reside preferentially at the top of the step edges (see Supporting Information). This is due to the Smoluchowski effect, which creates a charge redistribution that leaves the top of the step edge slightly electropositive and the bottom electronegative.<sup>32</sup> The electron-rich sulfur atom at the center of the dibutyl sulfide molecule presumably binds most strongly to the upper part of the step edge. It is interesting to note that, as dibutyl sulfide assembles preferentially at step edges at 78 K, it must be mobile on the Cu{111} surface at

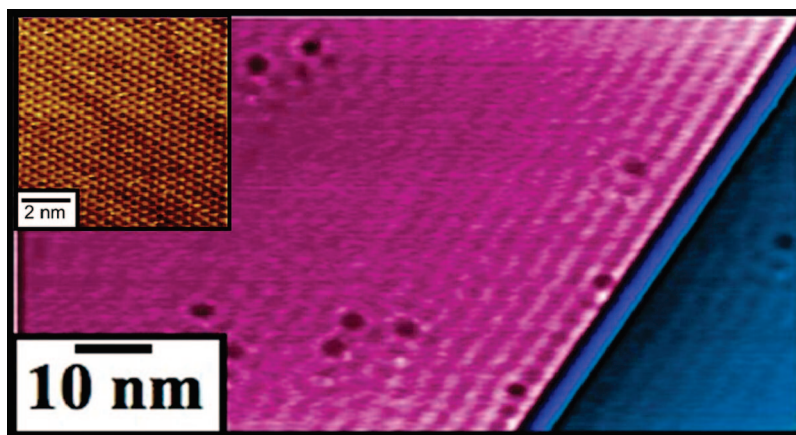


Figure 1. STM image of a clean Cu{111} surface with several point defects and a step edge at 78 K. Color contrast allows visualization of the standing waves emanating from the step edge and defects. Image conditions:  $V_{\text{tip}} = -0.05$  V,  $I = 1$  nA. The inset shows atomic resolution of clean Cu{111} at 78 K. Image conditions:  $V_{\text{tip}} = -0.02$  V,  $I = 300$  nA.

this temperature. This point will become pertinent once we discuss the molecule's behavior at higher coverage.

Once all the adsorption sites at step edges are filled, dibutyl sulfide begins to form ordered islands on the Cu terraces. Figure 2 shows an STM image of 0.5 ML of dibutyl sulfide, in which it can be seen that these islands are linear and point preferentially in three directions, 120° from each other. The proposed internal structure of these islands is shown schematically in the inset of Figure 2. The molecules lie parallel to one another, and the linear islands are one molecule thick. Further evidence for this packing structure in the form of high-resolution images will be presented later in this paper. Two STM "movies" of such an area are available with Figure 2 in the Web version of this article. These movies consist of a series of STM images taken 2 min apart over ~12 h and reveal that the length of the islands changes over time, but their width remains constant. The changes in island length over time originate

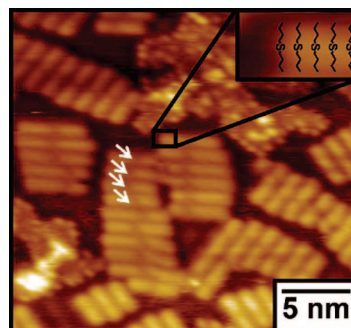


Figure 2. STM image of 0.5 ML surface coverage of dibutyl sulfide on Cu{111} at 78 K. Individual dibutyl sulfide molecules are aligned in linear islands that point in three preferred directions. The white arrows indicate the position of faint depressions that occur in places where the rows of molecules are offset. The inset shows a model of the molecular packing in one chain. Image conditions:  $V_{\text{tip}} = 0.9$  V,  $I = 2$  pA.

Two STM movies, video 1 and video 2, of dibutyl sulfide island dynamics at 78 K are available.

from individual molecules desorbing from the ends of the islands and re-adsorbing on other islands. The fact that the length of dibutyl sulfide islands but not the width changes over time supports the proposed structure of the islands consisting of individual molecules packed parallel with their long axes perpendicular to the long axes of the islands.

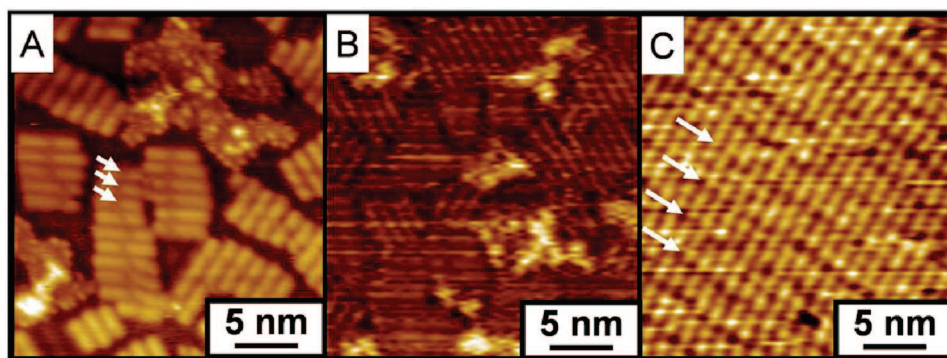
It is interesting to note that, over many hours of monitoring the same group of islands, their lengths changed dramatically, but never the overall orientation of the islands. This hints that individual dibutyl sulfide molecules are free to desorb from the ends of the islands, move around the terraces in a 2D gas state, and reattach to other islands.<sup>33,34</sup> However, the islands themselves are stable, and their overall position remains constant over time. The islands derive stability from both molecule–surface (dative) and molecule–molecule (van der Waals) interactions. This explains why desorption from islands occurs only at the ends: this requires breaking only one intermolecular van der Waals bond, whereas desorption from the middle of the island would require breaking two bonds. The upper area of Figure 2 contains a disordered region where the molecules can be imaged but do not appear to be ordered. These areas account for  $\sim 5\%$  of the total surface area. We suggest that these areas contain aggregates of dibutyl sulfide molecules in a disordered array. We never observed scattering of surface-state electrons from the dibutyl sulfide islands, even though we imaged at a wide variety of tip biases between 0.05 and 1 V. We believe that the 2D gas of dibutyl sulfide molecules present on the surface (as seen in the STM movies accompanying Figure 2) obscured any subtle image contrast arising from standing waves.

Figure 3 shows the effect of increasing the surface coverage of molecules to 1 ML and performing a brief anneal by removing the sample from the STM stage and placing it into a sample holder at the edge of the STM UHV chamber at room temperature for 2 min. The temperature attained during this

procedure was calculated from thermal diffusion studies of dimethyl sulfide on Cu{111} to be  $120 \pm 20$  K.<sup>35</sup> These diffusion studies involved adsorbing dimethyl sulfide on Cu{111} at a surface temperature of 7 K. STM imaging revealed a homogeneous distribution of molecules over the surface. The sample was then removed from the cooled STM stage and placed in the room-temperature holder for 2 min. After the sample was recooled to 7 K, STM imaging revealed that the molecules were no longer randomly distributed over the terraces; rather, bare areas above step edges measuring 16 nm in width were observed. This indicated that, during the brief warming, molecules were able to diffuse an average distance such that those near step edges became trapped at the step, leaving a patch 16 nm wide above every step edge. Using a random walk model in which the molecules take steps equal to one atomic spacing, an Arrhenius expression with a pre-factor of  $10^{12}$  Hz was used to solve for the average temperature of the anneal. The energy barrier to diffusion was assumed to be equal to roughly one quarter of the desorption enthalpy.<sup>36,37</sup> This calculation yielded an annealing temperature of  $120 \pm 20$  K, with the large error range accounting for the various assumptions. Coadsorption of impurities during the 2 min annealing procedure was not a problem, as the UHV chamber base pressure was  $2 \times 10^{-11}$  mbar. Even with a sticking probability of unity, the total impurities adsorbed during such a 2 min anneal would be  $\sim 0.001$  ML.

STM images of 0.5 and 1 ML of dibutyl sulfide before annealing to 120 K are shown in Figure 3A,B. These images reveal that the surface consists of a collection of ordered islands pointing preferentially in three directions. At 1 ML coverage (Figure 3B), it can be seen that the irregular-shaped areas between the ordered islands contain disordered arrays of dibutyl sulfide molecules that do not have enough space to pack in a regular fashion. Figure 3C illustrates that a striking transformation has occurred in the 1 ML dibutyl sulfide layer upon

the sample warming to 120 K. The image shows a very ordered surface layer consisting of a single rotational domain with a missing molecule defect at the bottom of the image. It is clear from these data that, at 120 K, the molecules do not have enough energy to desorb from the surface, but they do reorder significantly. This is in contrast to the behavior of the dibutyl sulfide islands at 78 K, in which individual molecules at the



**Figure 3.** Effect of surface coverage and annealing on the ordering of dibutyl sulfide on Cu{111}: STM images of (A) 0.5 ML coverage at 78 K, (B) 1 ML coverage at 78 K, and (C) the 1 ML surface after annealing at  $120 \pm 20$  K for 2 min. It is obvious that the many smaller domains have coalesced into a single domain. The white arrows in panels A and C indicate areas where the molecular rows are offset. Image conditions:  $V_{\text{tip}} = 0.9$  V,  $I = 10$  pA.

ends of the linear islands were found to desorb and re-adsorb, but the islands kept their overall orientation on the surface.

It is also obvious from Figure 3 that the SAM resulting from annealing 1 ML of dibutyl sulfide at 120 K is perfectly ordered, has only a single defect in the 125 nm<sup>2</sup> area imaged, and contains no etch pits. In fact, single rotational domains measuring in excess of 10 000 nm<sup>2</sup> were routinely observed after this annealing procedure. Disordered areas like those shown in Figure 2 were never observed in films that had been annealed at 120 K.

Another interesting feature is observed in the images in Figure 3. In Figure 3A, a faint depression can be seen near the center of each dibutyl sulfide island (as highlighted by white arrows). In Figure 3C, these same faint depressions are seen running through the whole image. Unfortunately, the quality of the image in Figure 3B is not sufficient to see these fine details. The origin of these features was revealed by high-resolution imaging. Figure 4 shows an STM image of 1 ML coverage of dibutyl sulfide, recorded in an area similar to that shown in Figure 3C. With this tip state, each molecule is imaged as a protrusion between two depressed lobes. The protrusions correspond to the sulfur atoms of the dibutyl sulfide molecules. This assignment is based on previous STM imaging of ethers and thioethers that revealed that the O and S atoms in ethers and thioethers image with more contrast than the alkyl tails.<sup>21,22</sup> It is interesting to note that, in 90% of our STM images, dibutyl sulfide appeared as oblong protrusions with no internal features. On occasion, the STM tip would pick up a weakly bound molecule and yield very high resolution images in which submolecular features could be observed. In these images, the S atom appeared as a protrusion between the two alkyl chains.

It can be seen from Figure 4 that the molecules pack in straight rows of six or seven molecules before being offset sideways to begin another straight row. This pattern is repeated throughout the whole overlayer in the annealed structure shown in Figure 3C, and it appears that the as-formed islands in Figure 3A also have a single offset of the molecules near the center of each island. In the larger-scale images, these offsets appear as faint depressions. It is also interesting to note that the row offsets are correlated to adjacent rows. This supports our conclusion that these features correspond to a sideways shift of the rows, as every offset of a row of molecules will put lateral "pressure" on the adjacent rows, causing them to shift also. Packing structures similar to the ones observed here, in which long-chain molecules lie flat on the surface and parallel to one another, have been observed previously in a variety of self-assembled systems involving alkanes, alcohols, and acids on HOPG.<sup>8–10</sup>

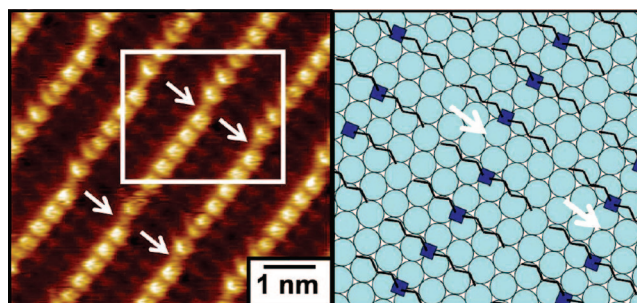


Figure 4. (Left) Molecular resolution of 1 ML of dibutyl sulfide on Cu{111} at 78 K. Each bright protrusion is the sulfur atom within the dibutyl sulfide molecule. Image conditions:  $V_{\text{tip}} = -0.01$  V,  $I = 10$  pA. (Right) Proposed model of the adsorption sites of the dibutyl sulfide molecules in the white box in the STM image on the left. The pale blue circles represent the positions of the Cu atoms of the substrate. The navy blue squares indicate the adsorption site of the S atoms, and the white arrows show the position at which the rows are offset.

The packing dimensions of dibutyl sulfide on Cu{111} were measured from high-resolution images of the type shown in Figure 4 and compared to the dimensions of the Cu{111} atomic lattice underneath in order to determine the overlayer structure of dibutyl sulfide. As can be seen in the left panel of Figure 4, the dibutyl sulfide molecules line up in groups of seven or eight before shifting sideways and beginning a new row. These rows were always aligned along the  $[1\bar{1}\bar{2}]$  direction. The spacing between dibutyl sulfide molecules in the rows was  $0.39 \pm 0.03$  nm, and the rows shifted across by  $0.17 \text{ nm} \pm 0.03 \text{ nm}$  and up by  $0.56 \text{ nm} \pm 0.03 \text{ nm}$  every seven or eight molecules. The distance between adjacent rows was  $1.27 \pm 0.03 \text{ nm}$ . After lengthy consideration of different packing models and comparisons to the experimental data, we propose an over-

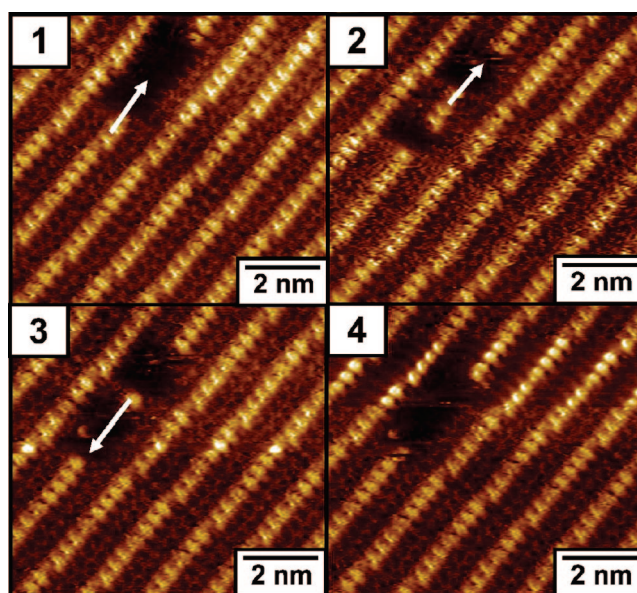
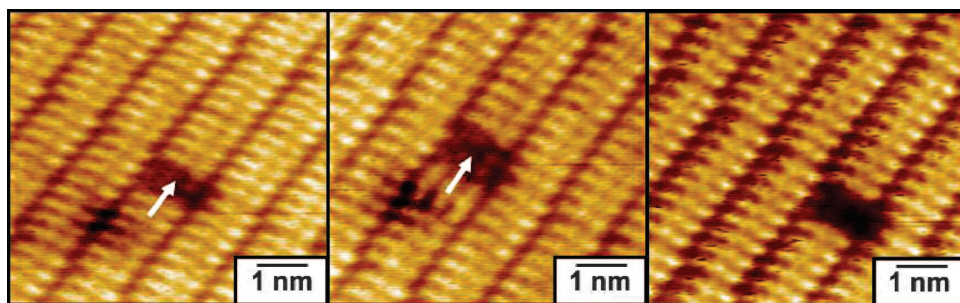


Figure 5. Molecular abacus: molecular manipulation of individual dibutyl sulfide molecules in an ordered domain on Cu{111} at 78 K. The small yellow protrusions in the STM images are the S atoms of each dibutyl sulfide molecule. The arrows indicate the manipulation traces of the STM tip during this sequence of movements. Image conditions:  $V_{\text{tip}} = -0.01$  V,  $I = 10$  pA. Movement parameters:  $V_{\text{tip}} = 0.02$  V,  $I = 150$  nA.



**Figure 6.** Reversibly switching the orientation of three dibutyl sulfide molecules within a highly ordered island on Cu{111} at 78 K. The arrows indicate the trace of the STM tip during molecular manipulations. Image conditions:  $V_{\text{tip}} = 0.01$  V,  $I = 10$  pA. Movement parameters:  $V_{\text{tip}} = 0.02$  V,  $I = 150$  nA.

layer structure as shown in the schematic in the right panel of Figure 4. The molecules all sit in three-fold hollow adsorption sites. The molecules in the rows sit a distance of  $\sqrt{3}d_{\text{Cu}}$  ( $d_{\text{Cu}}$  is the diameter of a Cu atom, 0.256 nm) from each other. The rows are separated by a distance of  $5d_{\text{Cu}}$ , and the rows move to the side by  $0.5d_{\text{Cu}}$  and up by  $2.15d_{\text{Cu}}$ . The reason the proposed model involves three-fold hollow adsorption sites is that atop adsorption would give a distance between rows of 0.66 nm, in disagreement with the experimental finding of  $0.56 \pm 0.01$  nm. A model involving bridge adsorption sites was also considered but led to a difference of  $>20\%$  in the distance by which the rows shift upward.

We note that the biggest discrepancy in our model is the deviation of the molecule–molecule separations within the rows compared to that expected from the  $\sqrt{3}d_{\text{Cu}}$  distances, an 11% mismatch. Inspection of the high-resolution images, like that shown in the left panel of Figure 4, reveals that the molecules are not regularly spaced in the rows; rather, three or four molecules appear at regular  $0.39 \pm 0.03$  nm spacing, and the other three molecules appear with either smaller or larger separations. We postulate that the ideal separations for dibutyl sulfide on Cu{111} are slightly shorter than the  $\sqrt{3}d_{\text{Cu}}$  distance; therefore, molecules pack in a semiregular fashion within each row, matching most closely to the  $\sqrt{3}d_{\text{Cu}}$  distance. The energy lost in perturbing each molecule from its three-fold hollow site is offset by the stability gained by increased van der Waals interactions between the molecules.

In order to further probe the structure and stability of dibutyl sulfide molecules in the ordered overlayers, we performed molecular manipulation experiments.<sup>38–43</sup> These experiments involved imaging an area and then manipulating individual molecules in that area by reducing the tip voltage ( $V_{\text{tip}} < 0.02$  V) and increasing the tunneling current ( $I > 150$  nA) in order to bring the tip very close to the molecule to be moved. An automated program then moved the tip to a new location before the gap conditions were returned to the original imaging conditions.

Figure 5 shows an area of nearly 1 ML coverage of dibutyl sulfide with a vacancy (approximately eight missing molecules) in the upper left part of the image

(panel 1). The white arrows in the images show various tip traces during the manipulation sequence. First, three molecules were moved simultaneously up into the center of the vacancy (panel 2). Then, two of those molecules were moved to the upper end of the vacancy, leaving behind a single molecule (panel 3). Finally,

the single molecule in the center of the vacancy was moved back down to the lower end of the vacancy (panel 4). Almost all molecular manipulation experiments to date have been performed on low surface coverages of molecules.<sup>38–43</sup> Our results demonstrate that molecules inside a densely packed monolayer can be reproducibly manipulated, providing a vacancy is present. These results also demonstrate that more than one molecule can be moved with a single manipulation experiment, exactly analogous to an abacus. A similar “molecular abacus” was constructed by Cuberes *et al.*, in which  $C_{60}$  molecules adsorbed at a step edge on Cu{111} were moved back and forth, one molecule at a time.<sup>44</sup> It is interesting to note that, in our system, it is possible to move more than one molecule at a time, just as more than one bead of an abacus can be moved back and forth on the rail. This is most likely due to the fact that the molecules are manipulated in the confined space of a vacancy surrounded by walls of a regularly packed array of dibutyl sulfide molecules. The surrounding molecules impose a potential barrier on each side of the molecules being manipulated, thus only allowing them to move linearly back and forth. Therefore, the tip can move many molecules by forming a strong contact with a single molecule that in turn pushes or pulls others with it. The extra molecules are guided into position by the molecular rows on each side of the vacancy. This type of multiple molecule manipulation is not possible on surfaces with a low coverage of molecules, as there is no confining potential that allows for reproducible manipulation.<sup>45</sup> Care was taken during the manipulation experiments to only move molecules at the edge of a vacancy. Moving the tip over the film with manipulation parameters of 0.02 V and 150 nA resulted in disruption of the ordered molecular packing in the area directly underneath the tip trace.

In an effort to decipher whether the tip was pushing or pulling the molecules, tip height vs distance curves were recorded during the manipulation steps. Bartels *et al.* demonstrated that different systems produced different tip height vs distance curves, depending on whether the tip was pushing, pulling, or sliding the adsorbate.<sup>40</sup> The authors found that these height vs distance traces were regular sawtooth patterns, and

from their orientation the authors could elucidate the manipulation mechanism. Our traces were fairly featureless, with occasional spikes and dips, and did not contain regular sawtooth patterns; therefore, we could not conclude by which mechanism the tip moved the molecules.

We discovered that molecules could also be reversibly rotated in and out of a vacancy. Figure 6 shows that, during an attempt to move molecules up into a vacancy, all three molecules were rotated by 90°. A further single manipulation step rotated the molecules back parallel to the others and returned them to the upper end of the molecular row. The fact that all three molecules were rotated simultaneously demonstrates the importance of van der Waals interactions in keeping the molecules aligned. This result also corroborates the earlier proposed packing structure, in which the positions of the molecules were found to be slightly perturbed from the epitaxial  $\sqrt{3}d_{\text{Cu}}$  spacing in order to maximize their van der Waals interactions. It appears that these forces play an important role in the assembly of thioethers, even in molecules with tails that are only four carbon units long.

Manipulations were performed on a variety of nearly 1 ML surface coverages in an attempt to gain control of lateral versus rotational motion. In around 70% of manipulation experiments, molecules could be moved back and forth across a vacancy without rotation. In the other 30% of cases, the tip caused the manipulated molecules to rotate 90° and lie sideways in the vacancy. This effect occurred randomly; however, further manipulations were usually successful in rotating the molecules back to their original angles and positions within the vacancy.

## CONCLUSIONS

By studying a simple thioether system, dibutyl sulfide on Cu{111}, we have elucidated several important aspects of thioether self-assembly:

1. Dibutyl sulfide adsorbs intact on Cu{111} at 78 K.
2. The molecule is mobile enough at 78 K to locally order in very regular arrays of linear islands that maximize both Cu-S and intermolecular van der Waals interactions.
3. At  $\sim 0.5$  ML coverage, the surface contains an array of islands oriented in only three different directions that correlate with the  $[1\bar{1}\bar{2}]$  directions of the Cu{111} substrate.
4. Annealing at  $120 \pm 20$  K produces a surface with very large domains of regularly packed dibutyl sulfide molecules in a local  $5 \times \sqrt{3}$  rectangular unit cell.
5. These large domains are free of defects like etch pits and rotational boundaries.
6. Molecular manipulation is capable of manipulating up to three dibutyl sulfide molecules at a time inside ordered arrays of the molecule, providing vacancies are present.

These data suggest that thioethers are capable of forming very well ordered SAMs that are free of some of the defects associated with thiol-based SAMs. Thioethers are less susceptible to oxidation, and the fact that they form very ordered arrays free of etch pits and rotational domain boundaries means that they contain fewer “weak spots” where attack and degradation can occur. While this was a low-temperature study involving a small molecule, we believe that these results are of general significance to thioether assembly. Longer thioether molecules have larger intermolecular van der Waals interactions and, therefore, are stable at room temperature.<sup>24–26,30</sup> We are now investigating the chain length dependence of the packing structure and the effect of adding end group functionality to the thioethers.

## METHODS

All experiments were performed in a low-temperature, ultra-high-vacuum (LT-UHV) scanning tunneling microscope (Omicron).<sup>46</sup> The very high stability of the microscope at 78 K allows us to study a particular area of the surface for many hours.<sup>47,48</sup> A Cu{111} single crystal was purchased from MaTeck and cleaned by cycles of argon ion sputtering (1 keV/10  $\mu\text{A}$ ) and annealing at 820 K. Dibutyl sulfide (99.9% purity) was obtained from Sigma Aldrich and was further purified by cycles of freeze/pump/thaw prior to introduction to the STM chamber via a leak valve. The molecule was deposited on the sample at 78 K by a collimated molecular doser while the tip was scanning. All coverages are quoted in monolayers, where 1 ML refers to a complete, single-layer coverage of molecules, with 1 dibutyl sulfide molecule per 10 surface Cu atoms.

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**Supporting Information Available:** An image of individual dibutyl sulfide molecules adsorbed at step edges. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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